

Preparation of copper nanoparticles by radiation

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Abstract Copper nanoparticles were successfully synthesized by ^{60}Co - γ radiation with aqueous solution of cupric sulfate under inert nitrogen-purged conditions. Cu nanoparticles were characterized by using X-ray diffraction (XRD), transmission electron microscopy (TEM), laser particle size distribution analyzer (LSPDA) and differential scanning calorimeter (DSC) techniques, respectively. The effects of solution system, pH, additive of surfactant and absorbed doses on the particle size and its distribution as well as stored stability of Cu nanoparticles were investigated. High resolution TEM pictures showed the formation of homogeneous cubic-structured copper nanoparticles with different sizes depends on the synthetic conditions. This new kind of synthesis method shows the excellent stability, which may provide an efficient way to improve the fine tuning of the structure and size of copper nanoparticles.

Key words ^{60}Co - γ radiation, Copper nanoparticle, Characterization

1 Introduction

Due to the unique properties of Metallic Cu, such as interesting optical, electronic, magnetic and chemical properties, Cu nanoparticles are widely used in the fields of lubrication additives, conductive paste, antibacterial agent, information storage, effective catalyst, photoelectricity, etc. The synthesis of copper nanoparticles can be performed by physical gas deposition, electrochemical deposition, decomposition of organic metal compounds, liquid phase reduction, hydrothermal and microemulsion methods and so on. A burst of research activities is reported in the area of synthesis and fabrication of different sizes and shapes of Cu nanoparticles. However, the reproductive method for synthesis of copper nanoparticles with a specific size and well defined surface composition with long storage time remain a challenging task. Very little work has been carried out on the cold synthesis of copper nanoparticles. We have attempted the synthesis of size-controlled copper nanoparticles through a simple aqueous system using ^{60}Co - γ radiation.

2 Experimental

2.1 Materials

CuSO_4 , AR, is from Chemical Co. Ltd. of Wenzhou. Isopropyl alcohol (IPA), AR, is from Shuanglin Chemical Co. Ltd. of Hangzhou. Absolute ethyl alcohol, AR, is from Damao Chemical Co. Ltd. of Tianjin. Polyvinyl alcohol (dynamic viscosity 54.0-66.0 $\text{mPa}\cdot\text{s}^{-1}$), AR, is from National Chemical Co. Ltd. 25% aqueous ammonia, CP, is from Dafang Chemical Co. Ltd. of Hangzhou. Acetic amine, AR, is from Hewei Chemical Co. Ltd. of Shanghai. Dodecyl mercaptan, CP, is from Shanghai Chemical Co. Ltd. of National Medicine Company. Sodium dodecyl benzene sulfonate (SDBS), CP, is from Guanghua Chemical Co. Ltd. of Shantou. NNHDA, dodecyl alcohol amine, CP, is from Yinghu Chemical Co. Ltd. of Hangzhou. Sodium carboxymethyl cellulose, CP, is from Chemical Co. Ltd. of National Medicine Company. Oleamide, CP, is from Shentong Chemical Co. Ltd. of Zibo. Oleic acid, CP, is from Shuanglin Chemical Co. Ltd. of Hangzhou.

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2.2 Facility and instruments

Irradiation was performed by 10⁵ Curie ⁶⁰Co-γ source at Irradiation Center Facility of Zhejiang University. The crystal phase was determined by use of X Pertpro (XRD, Cu K_α λ=1.541 Å). Morphology and particle size were measured by use of JEM-1230 transmission electron microscope (TEM). Particle size and its distribution were measured by use of NaNo ZS-90 (LSPDA) and the melting point of Cu particles with different sizes was used SDT Q600 (DSC). And KQ-50DA ultrasonic disperse instrument, TG20M centrifuge; DZF-6050 vacuum oven and 85-2 magnetic whisk were used for treatment of samples.

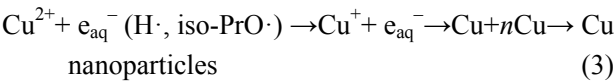
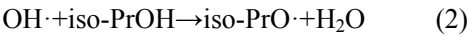
2.3 Preparing process of samples

Amount of aqueous solution of surfactant (PCM) was added in aqueous solution of CuSO₄, prepared by use of CuSO₄·5H₂O, under churn up condition and then amount of isopropyl alcohol was added as scavenger of OH· radical produced from radiolysis of water. The pH of the solution for irradiation was adjusted to be 6.5 by use of NH₄OH-NH₄AC and deoxygenated by bubbling with N₂ for 30 minutes. The irradiation for preparing Cu nanoparticles was performed by use of 10⁵ Curie of ⁶⁰Co-γ with different absorbed doses. The colour of solution was changed from blue into purplish red after irradiation.

The upper solution of irradiated sample was toppled out after centrifugal separation and then deactivation agent was added into remained solution to prevent the Cu nanoparticles from oxidation. After alternately several washes by use of deionized water

and absolute ethyl alcohol free from O₂ the sample was dried at 60°C and -0.01 Pa and stored in a small reagent bottle filled with high pure N₂ for further characterization.

The reduction of copper cations can be described as follow:



The radiolytical products of water, such as e_{aq}⁻, H^[1] can effectively reduce the cation of copper meanwhile the iso-PrO· formed from scavenging of OH· by isopropyl alcohol as shown in reaction (2) can also reduce it. Some Cu atoms accumulated to form a crystal and grew to form a nanoparticle^[2,3].

3 Results and discussion

3.1 Effect of surfactants on the properties and size of Cu nanoparticles

In order to make the decentrality and stability of Cu atoms formed in irradiated solution, different kinds of surfactants, such as polyving akohol, sodium dodecyl benzensulfate, polypropylene pyrrolidone, polyacryl- amide, Tween 80, sodium alginate and PCM, were used in the preparing solution with 1.0 g/100 mL surfactant, 0.05 mmol·L⁻¹ CuSO₄, 2 mol·L⁻¹ IPA, at pH adjusted by NH₄OH/NH₄AC for irradiation and the results were listed in Table 1.

Table 1 Results of sample with additive of different surfactants obtained after irradiation with absorbed doses of 100 kGy

Samples	Surfactant	Absorbed doses / kGy	Aspect of solution
1	Polyving akohol	100	Purplish red
2	sodium dodecyl benzensulfate	100	Purplish red
3	polypropylene pyrrolidone	100	Purplish red
4	polyacrylamide	100	Black bulk sediment
5	Tween 80	100	Black sediment
6	sodium alginate	100	Black sediment
7	PCM	100	Purplish red, stable

The colour of solution was all blue with additive of different surfactants before irradiation. In the sample 1, 2 and 3, Cu²⁺ could be reduced to form purplish red Cu nanoparticles^[4] under radiation. However, the solution got to become black within 20 minutes after irradiation, which meant that reduced Cu

was transferred into Cu₂O *via* oxidation in air condition. In sample 4, 5 and 6, the solution presented black and some black sediment were observed just after irradiation, which meant that the 3 kinds of surfactants could not protect reduced Cu from oxidation in radiation process and the particle might be

composition of Cu_2O or $\text{Cu}_2\text{O}+\text{Cu}$ ^[5]. In contrast, with the solution system by use of PCM prepared by our group the purplish red Cu nanoparticles with very excellent stability were obtained as the residues of the surfactant PCM had both carboxyl and amide groups,

which made the Cu nanoparticles with good distribution and protection from oxidation. Thus the surfactant PCM was always used for preparation of Cu nanoparticles in this study.

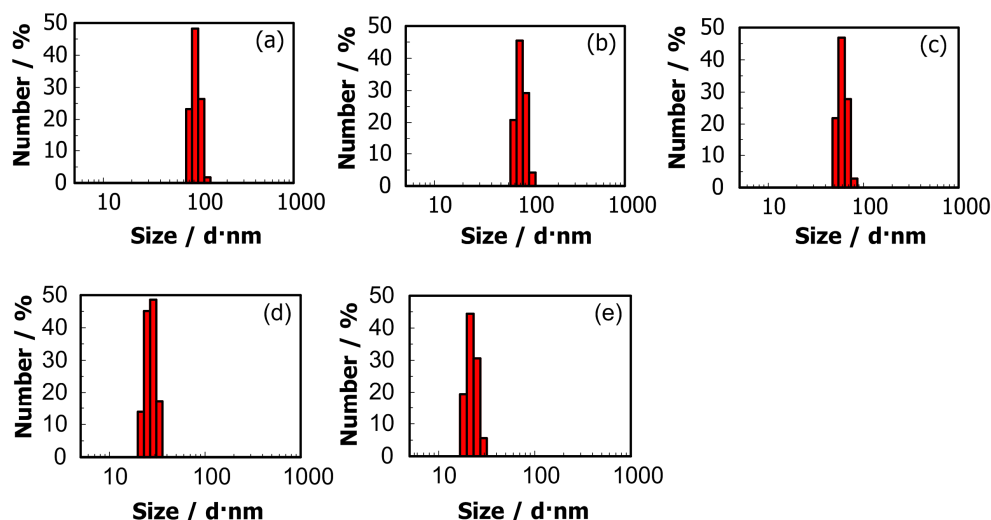


Fig.1 Particle sizes and distributions against the concentrations of PCM determined by LSPSDA: 0.6 g/100 mL (a), 1.0 g/100 mL (b), 1.4 g/100 mL (c), 1.8 g/100 mL (d) and 2.2 g/100 mL (e).

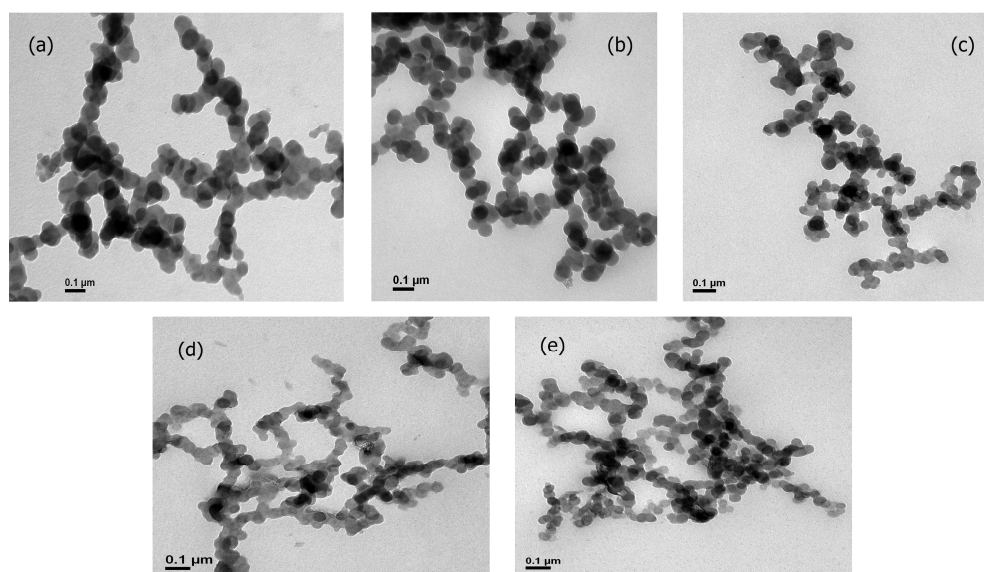


Fig.2 TEM spectra of Cu nanoparticles obtained with different concentrations of PCR determined by LSPSDA: 0.6 g/100 mL (a), 1.0 g/100 mL (b), 1.4 g/100 mL (c), 1.8 g/100 mL (d) and 2.2 g/100 mL (e).

The effect of different concentrations of surfactants on the Cu nanoparticle size was also investigated by characterization with LSPSDA and TEM. As shown in Figs.1 and 2, the particle sizes and distributions decreased with the increment of concentration of PCM and the sample presented circular and with good distribution. The average

particle size was 122.4 nm when the concentration of PCM was 0.6 g/100 mL, and it was 21.3 nm when the concentration of PCM was 2.2 g/100 mL. It can be supposed that the PCM absorbed on the surface of Cu nanoparticle might form electric double layer, which makes the particle very stable in the solution or air and protects it from oxidation^[6].

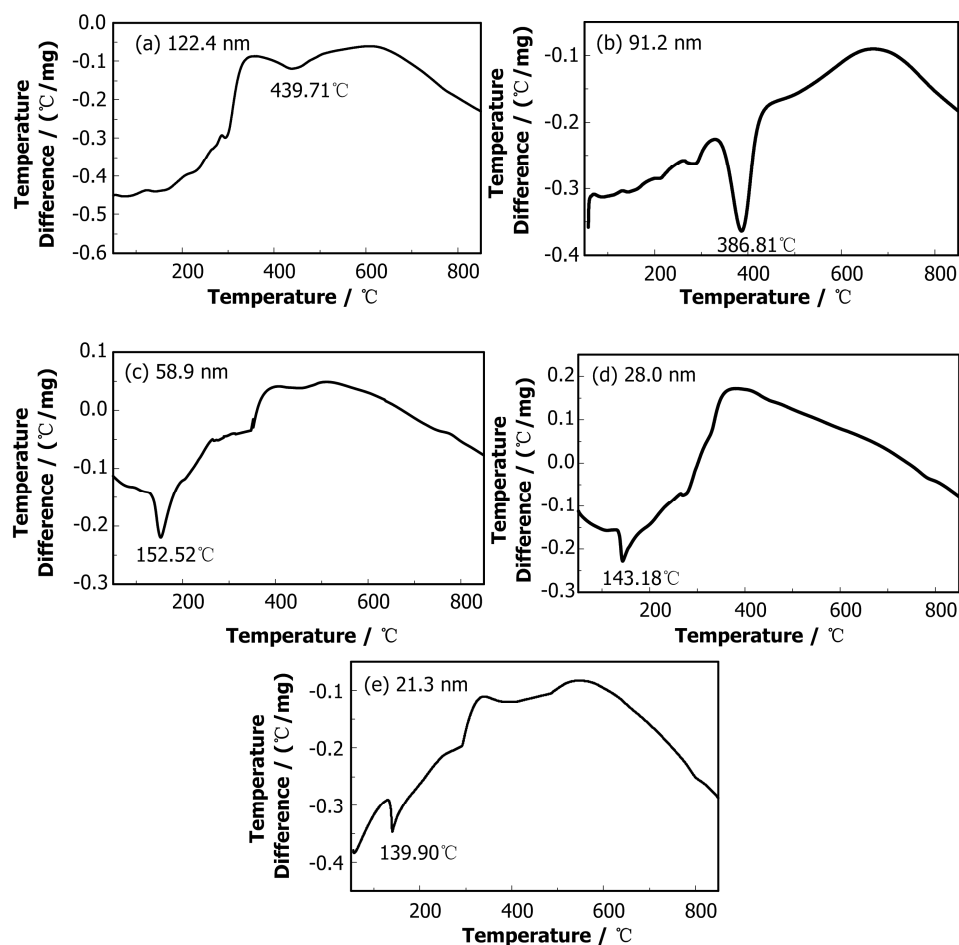


Fig.3 Melting points of Cu nanoparticles with (a) 122.4 nm, (b) 91.2 nm, (c) 58.9 nm, (d) 28.0 nm and (e) 21.3 nm measured by DSC.

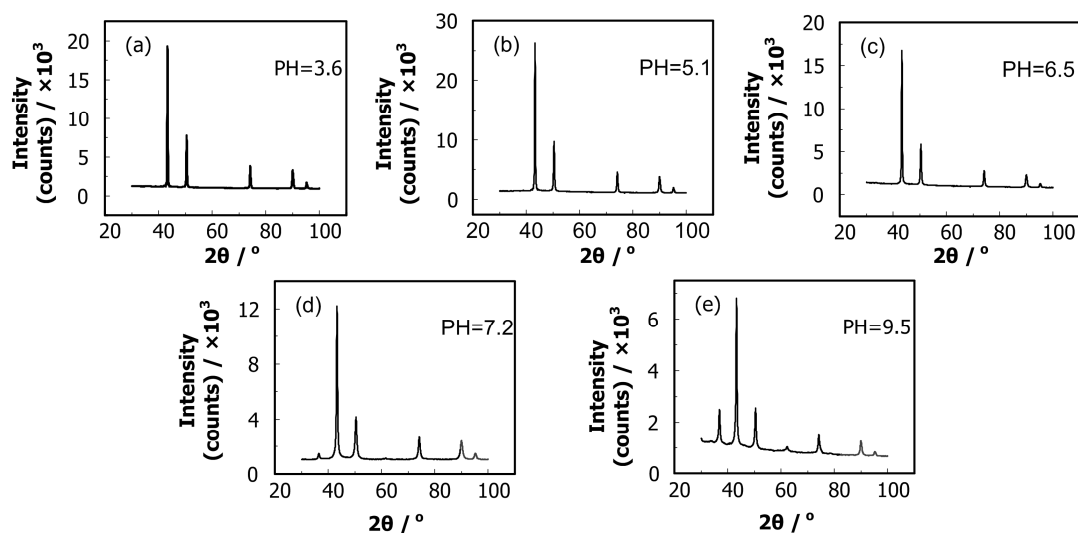


Fig.4 XRD spectra determined with Cu nanoparticles obtained at pH (a) 3.6, (b) 5.1, (c) 6.5, (d) 7.2 and (e) 9.5, respectively.

3.2 Relationship between the size and melting point of Cu nanoparticles

Generally, the melting point of material is defined as

the temperature at that the equilibrium between solid and liquid of pure material will occur at fixed pressure. And the change of free energy for transfer process of phase is suitable for the equation $\Delta G=0$. To the solid

of pure material with highest degree of dispersion, such as nanoparticle, its chemical potential must be related with its particle size^[7] though the potential is a function both of pressure and temperature. So the melting point of Cu nanoparticle with different particle sizes can be used to describe its properties.

Here, the DSC was used to determine the melting point of Cu nanoparticle with particle size of 122.4 nm, 91.2 nm, 58.9 nm, 28.0 nm and 21.3 nm, respectively. The results were shown in Fig.3.

As shown in Fig.3, along with the decrement of the particle size the melting point of Cu nanoparticles decreases. When its particle size is 122.4 nm its melting point is 439.71°C, and when the particle size is 21.3 nm and its melting point is 139.9°C, which is deeply lower than 1083.4°C of general Cu.

3.3 Effect of pH on the phase of Cu nanoparticles

The chemical property of Cu nanoparticles is very active as $E^0 \text{Cu}^{2+}/\text{Cu}=0.337 \text{ V}$. It means that there may be some Cu_2O exists in the Cu nanoparticle

formed from reduction of Cu^{2+} in solution induced by γ -rays. Of course, the pH of the solution may play important role in the reductive process. XRD was used to determine the phase of Cu nanoparticles obtained at pH of 3.6, 5.1, 6.0, 7.2 and 9.5, respectively.

As shown in Fig.4, the X-diffraction angles, 2θ , with samples of a, b, c and d are 43.53° , 50.24° , 74.91° and 89.88° , which are well according with standard X-diffraction angles of Cu listed in the card of 01-085-1326 as characteristic parameter. It can be indicated that the Cu nanoparticles formed with these pH are all composition of pure Cu. When the solution at pH of 7.2 and 9.5 was engaged, besides the X-diffraction angles of pure Cu, 2θ of 36.35° and 61.36° , according to the characteristic X-diffraction angles of Cu_2O listed in card of 00-005-0667, X-diffraction peak was also observed, which meant that Cu_2O exactly formed. And the amount of Cu_2O would increase with the increment of pH value. Anyway, there was no characteristic X-diffraction peaks of CuO in our study.

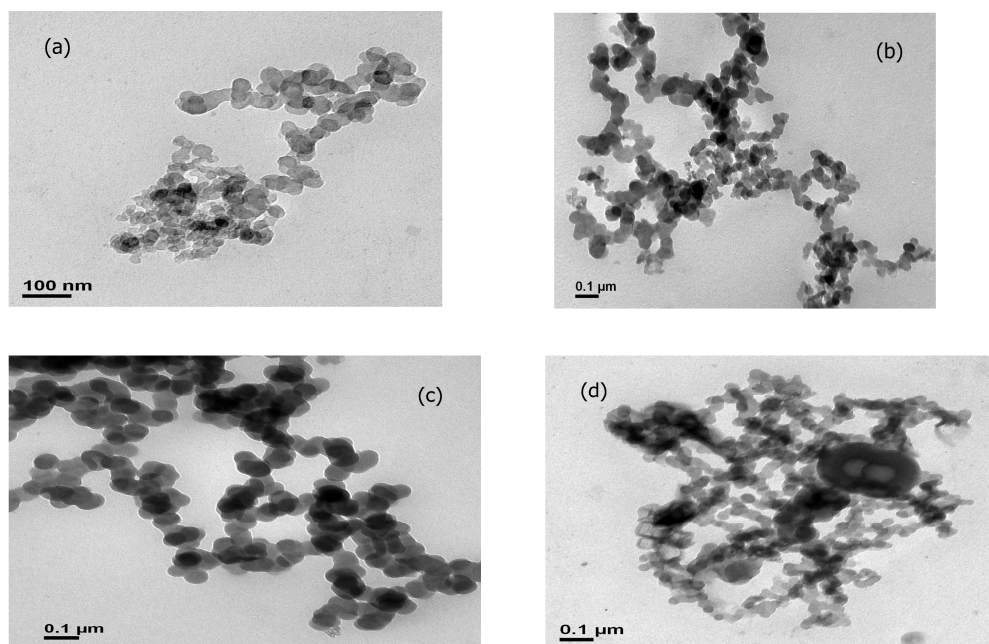


Fig.5 TEM spectra of Cu nanoparticles with different absorbed doses: (a) 50 kGy, (b) 150 kGy, (c) 300 kGy and (d) 500 kGy.

3.4 Effect of absorbed doses on the formation of Cu nanoparticles

As shown in Fig.5(a), the upper solution of irradiated sample with absorbed doses of 50 kGy remained blue after centrifugal separation, which meant that a part of Cu^{2+} had not been reduced completely. But the Cu

nanoparticles with good distribution and small particle size formed besides a little of them with non-complete particles could be observed. When the absorbed dose was 150 kGy, the colour of upper solution became transparent from amaranth of irradiated sample after centrifuging meanwhile the obtained Cu nanoparticles

revealed good distribution with small size as shown in Fig.5(b). However, as shown in Fig.5(c), some accumulation could be observed in obtained Cu nanoparticles from the sample irradiated with absorbed doses of 300 kGy, and the particle size became larger though the Cu^{2+} was completely reduced. When the absorbed dose was 500 kGy shown in Fig.5(d), there was serious accumulation in Cu nanoparticles. It can be deduced that surface electric charge of Cu nanoparticles modified by surfactant may lose because of radiolytical decomposition of surfactants at higher absorbed doses.

3.5 Effect of deactivation on the storage performance of Cu nanoparticles

The metallic nanoparticles can be easily oxidized in air, so the deactivation of Cu nanoparticles was made by use of six kinds of compounds, such as NNHDA $\{\text{C}_{11}\text{H}_{23}\text{CON}(\text{CH}_2\text{CH}_2\text{OH})_2\}$, dodecyl mercaptan,

stearic acid, oleic acid, oleamide and castor oil. The deactivated sample was then put in air or alcohol for storage and the diffraction peak of Cu_2O was detected by XRD to identify if the Cu nanoparticle was oxidized at different storage time.

In Fig.6, with the samples being free from any deactivation stored in air (a) or alcohol (b) for 5 days, the characteristic diffraction peaks at 2θ of 36.40 and 61.3 were observed and the peaks in air were higher than that in alcohol, which meant that a part of Cu nanoparticles were oxidized to Cu_2O , especially in the air. Accordingly, the samples deactivated by stearic acid (c), oleic acid (d), oleamide (e), castor oil (f) and NNHDA (g) were also found to be oxidized but that of NNHDA was weaker compared with others. Only the sample deactivated by dodecyl mercaptan (h) was without any characteristic diffraction peaks of Cu_2O as there were characteristic diffraction peaks of pure Cu ($2\theta=43.35, 50.49, 74.11$ and 89.88).

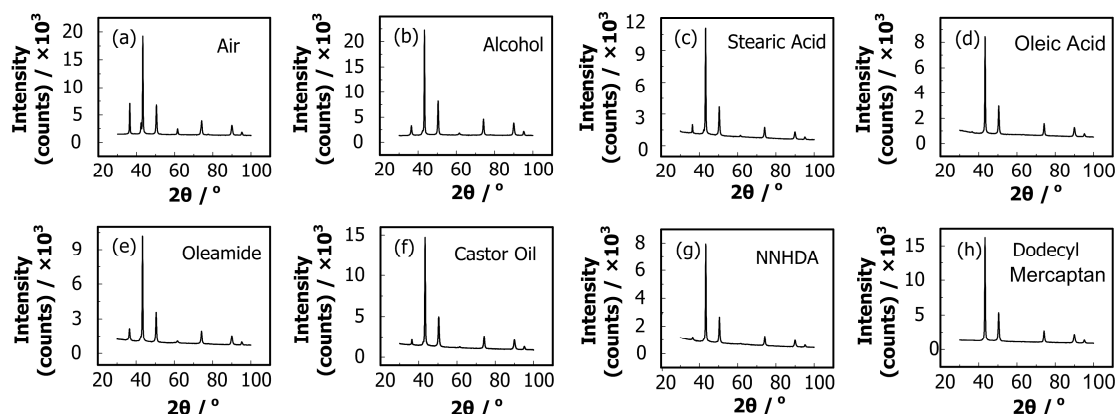


Fig.6 Diffraction spectra of Cu nanoparticles deactivated by different compounds stored in air or alcohol for 5 days characterized by XRD.

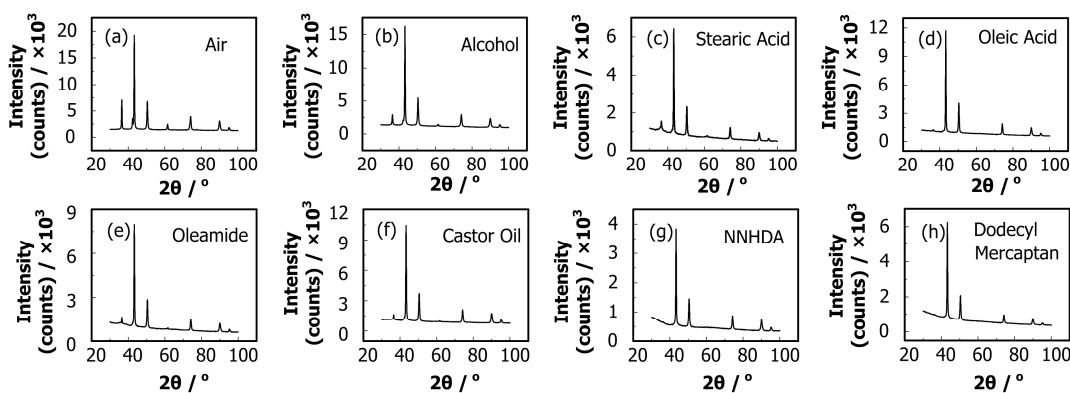


Fig.7 XRD spectra determined with the samples of Cu nanoparticles deactivated by NNHDA & dodecyl mercaptan and stored for 42 days.

When the storage time was set up 42 days in alcohol, the characteristic diffraction peaks of Cu_2O in the sample deactivated by NNHDA disappeared, which may be due to the reduction of Cu_2O by the active $\text{H}\cdot$ in molecule of NNHDA. However, the sample deactivated by stearic acid, oleic acid, oleamide and castor oil remained oxidized state except the sample deactivated by dodecyl mercaptan.

Considering that both of NNHDA and dodecyl mercaptan could effectively protect Cu nanoparticles from oxidation, prepared Cu nanoparticles were put into NNHDA and dodecyl mercaptan for storage test with 140 days and it was found that there was no characteristic diffraction peaks of Cu_2O with only that of pure Cu in the determination using XRD as shown in Fig.7. It means the two compounds can be used to protect Cu nanoparticles effectively. Compared with dodecyl mercaptan, NNHDA is soluble in water, free of poison and cheaper so it has been selected to protect Cu nanoparticles from oxidation and keep them for further study and application.

4 Conclusion

The Cu nanoparticles can be prepared by irradiation of CuSO_4 aqueous solution at room temperature without any additive. The determination using XRD, TEM and DSC has been revealed that samples of Cu nanoparticles with colour amaranth, particle size less than 100 nm and melting point of 139.90°C are globe powder of pure copper.

The surfactants of PCM added in reaction

system can make the Cu nanoparticles with good dispersal and the particle size decreases with the increment of concentration of PCM, which can be used to control the particle size and its distribution.

The effect of pH of reaction system on the formation of Cu nanoparticles has been investigated. It is better that preparing Cu nanoparticles should be performed in the pH range of 4.0–6.5 since Cu_2O will form if $\text{pH} > 7.2$ and the reduction of Cu^{2+} cannot be completed if $\text{pH} < 4$.

The absorbed doses for preparing Cu nanoparticle are in the range of 150 kGy–250 kGy. NNHDA, as deactivation agent, can protect Cu nanoparticles from oxidation even when the storage time was more than 140 days. And the productivity of Cu nanoparticles is 89%.

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